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Gas Chromatographic/Fourier Transform
Infrared Analysis of Trace Organics
Feasibility of Analysis after Collection of
Organics on TENAX-GC Sorbent Cartridges

Duke Univ., Durham, NC

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**GAS CHROMATOGRAPHIC/FOURIER TRANSFORM
INFRARED ANALYSIS OF TRACE ORGANICS:**

**Feasibility of Analysis after Collection of Organics
on TENAX-GC Sorbent Cartridges**

by

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature of processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

In most cases organics in ambient air can be identified by appropriate gas chromatographic (GC)/mass spectrometric (MS) methods in which a combination of retention time and mass fragmentation patterns often uniquely identifies a specific compound. Fourier Transform Infrared Spectrometry (FTIR) used as a substitute detector, i.e., GC/FTIR, or as a supplementary detector, i.e., GC/FTIR/MS, can distinguish some isomeric compounds by their unique infrared spectra and can as well, supplement mass spectral data. However, FTIR detectors lack the sensitivity necessary to directly detect ambient air concentrations of trace pollutants without preconcentration. In this study compounds of interest are preconcentrated by collection on TENAX-GC sorbent cartridges, and the feasibility for GC/FTIR detection and identification of these compounds desorbed from the cartridges is examined.

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ABSTRACT

An analytical system consisting of a Varian Model 3700 gas chromatograph (GC) equipped with a capillary column was interfaced with an IBM 9195 Fourier transform infrared (FTIR) spectrometer to investigate the feasibility of detecting volatile organics, in particular isomeric species. Samples were introduced by desorption from TENAX-GC sorbent tubes. Infrared absorption by water vapor was identified as a problem and reduced by the use of a dryer unit between the desorption chamber and the GC column. Background subtraction of co-added spectra corresponding to sections of the Gram-Schmidt plot immediately adjacent to a peak further minimizes the effect of water vapor interference.

A synthetic sample mixture consisting of 380-575 ng per compound loadings of the gases m-, p-, o-xylene; m-, p-, o-chlorotoluene; and m-, o-dichlorobenzene was used to test the system. Identifications were made using the Sadtler IRVAP 8 x 16 spectral library and the associated search program. The correct isomer was identified among the ten most likely compounds for the chlorotoluenes, dichlorobenzenes and for o-xylene, while none of the other compounds or isomers in the sample was in this set of ten in any case. The two isomers m- and p-xylene co-eluted to the extent that their identification was not possible without further treatment of the data. Thus, with the exception of the two co-eluting isomers, the method discriminated clearly between all the isomeric species in the sample. Although, m- and o-dichlorobenzene and m-chlorotoluene were each hit number one, p-chlorotoluene was hit number two, o-chlorotoluene was hit number seven and o-xylene, hit number ten in the respective searches, identification beyond all reasonable doubt would require independent confirmation. Samples consisting of other multicomponent mixtures were also analyzed. Methods for lowering the detection and identification limits to less than 100 ng per compound per cartridge are proposed.

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SECTION 1

INTRODUCTION

The analysis of trace organic pollutants usually requires the concentration of the ambient sample prior to introduction into an analytical system. This is partially due to the relatively low ambient concentrations of the components of interest (typically in the ng/L range) and the relatively high detection limits of most analytical techniques. One method for the preconcentration of ambient trace organic pollutants is collection of the gaseous components on a solid sorbent. A common solid sorbent in current use is TENAX-GC. TENAX-GC is a porous polymer, poly(para-2-6-diphenyl-phenylene oxide),¹ that exhibits a wide range of applicability for collection of priority pollutants.² The desirable traits of TENAX-GC for collection of volatile pollutants include: high collection efficiencies, high breakthrough volumes, low decomposition or polymerization of sample during collection and low affinity for water.³ Due to its high thermal stability and low background bleeding at elevated temperatures, TENAX-GC is also well suited for the transfer of the adsorbed sample to the analytical system by thermal desorption.⁴ However, as is evident in the recent research by Pellizzari et. al.⁵ and Walling⁶, there are a number of potentially complicating factors related to the use of TENAX-GC, such as artifact formation, inadequate blank corrections, etc. This report is not concerned with these factors, but with the analysis of compounds retrieved from the TENAX-GC after sample loading.

TENAX-GC, and most sorbents, have many of the properties of chromatographic stationary phases. Thus, some compounds will be preferentially retained on the sorbent and the rates of elution (or thermal desorption) will vary from compound to compound. This complicates the transfer of the sample to the analytical system, since it would be desirable to introduce all the components of the sample into the analytical system simultaneously. This can be accomplished by cryogenically trapping the sample following thermal desorption.⁴ The cryotrap can then be rapidly heated (flushed), thus introducing the sample into the analytical system as a "plug". The thermal desorption/cryotrapping technique is widely used and has

been coupled to gas chromatographs and GC/MS systems for the separation and identification of the trace components present in ambient samples.⁷

In principle GC/FTIR should be complementary to GC/MS for the analysis of complex mixtures of volatile organic pollutants. Whereas GC/MS can often give molecular weights, provide information leading to an empirical formula, and provide some information about molecular structure, this information is in some cases insufficient to enable precise structural identification; this is particularly true for geometrical isomers. GC/FTIR, on the other hand, is capable of identifying structural patterns of molecules and providing information about the functional groups present. By nondestructively probing the vibrational frequencies of molecules it often affords a means of precise determination of structural formula. This capability of GC/FTIR to identify specific isomers not identifiable by GC/MS has been illustrated, for example, in the analysis of industrial wastewater extracts⁸ where it was shown that o-, m-, and p-dichlorobenzene isomers were identified by GC/FTIR, even though the three components co-eluted from the GC column. In addition, substitution patterns for dichloronitrobenzenes were identified. Gurka and Betowski⁹ also demonstrated the feasibility of GC/FTIR for the identification of aromatic isomers. In particular, tetrachlorobenzene isomers were identified. However, it was found that alkanes were difficult to identify by GC/FTIR. Shafer *et al.*¹⁰ also reported a detailed comparison of GC/FTIR and GC/MS for the analysis of a hazardous waste sample. GC/MS was found to be very useful for the identification of parent alkanes and alkylated aromatics, but had difficulty in distinguishing between positional isomers. In contrast, a large number of positional isomers of substituted benzenes were identified by GC/FTIR.

Shafer *et al.*¹¹ showed that in general, GC/FTIR shows more selectivity for polar compounds while GC/MS selectivity favors nonpolar compounds. It was also found that GC/FTIR is more sensitive for polar compounds (e.g., phthalates) than for nonpolar compounds (e.g., polycyclic aromatic hydrocarbons). However, relative sensitivities for GC/MS were more nearly the same for polar and nonpolar compounds. Gurka *et al.*¹² found that GC/FTIR is most sensitive for aliphatic and aromatic compounds containing carbonyl or other oxygenated functional groups and is least sensitive for

alkyl halides and aromatic hydrocarbons. In general, the relative sensitivity of GC/FTIR for a series of compounds is related to the absorption strength of the functional groups. Although GC/MS (with claimed minimum detection limits in the sub-nanogram region) is inherently much more sensitive than on-the-fly GC/FTIR, the background level of environmental samples can often limit the practical detection limits of GC/MS to 10-50 ng per component.⁸ This is comparable to the present claimed detection limits of GC/FTIR.¹³ Nevertheless, for actual samples of environmental importance, the detection limits for GC/FTIR have been found to be an order of magnitude higher than GC/MS.¹⁰ In general, it has been found that when a positive identification cannot be made, GC/FTIR more often reveals functionality. In many cases the combined use of both techniques enables positive identification not afforded by either technique alone.

The purpose of the project described in this report was to evaluate the feasibility of using on-the-fly GC/FTIR to detect and identify volatile organics adsorbed on TENAX-GC cartridges. Azarraga and Potter¹⁴ have described a GC/FTIR system which can utilize many different techniques of sample introduction, including thermal desorption from an adsorbent cartridge or a cold trap. In that particular study, charcoal was used as the solid sorbent. A test mixture containing a number of priority pollutants was used to illustrate the technique. However, the integration of thermal desorption/cryotrapping techniques using TENAX-GC as the solid sorbent, and on-the-fly GC/FTIR, has not been reported. While the two techniques (thermal desorption/GC and GC/FTIR) have been separately utilized for the analysis of organic pollutants, it is not obvious that all three techniques may be successfully combined. The primary goal of this project was to determine the feasibility of such a combination by analyzing well characterized laboratory-generated sample cartridges. Sample cartridges were loaded with realistic amounts (with respect to concentrations found in ambient samples) of various mixtures of organic compounds. Special emphasis was given to the identification of geometrical isomers. Instrumental problems addressed include removal of interferences due to co-eluting water, spectral cleanup to facilitate library based identifications, and development of an analytical method to coordinate the various instrument subsystems necessary for precise analyses.

SECTION 2

CONCLUSIONS

An analytical system consisting of a Varian Model 3700 gas chromatograph (GC) equipped with a capillary column and interfaced with an IBM Model 9195 Fourier transform infrared (FTIR) spectrometer can be used to distinguish between isomeric species. To accomplish this, water vapor in the sample must be essentially eliminated to prevent interference in the spectral identification of compounds. A Perma-Pure dryer (MD-125-48T) is being used for this purpose; however, its use restricts sample analysis to non-polar compounds. Significant additional improvement was obtained by subtracting the co-added spectra from immediately adjacent positions in the Gram-Schmidt plot, from the target compound spectrum.

At its present stage of development, the system has been used to discriminate among isomers in a synthetic sample mixture consisting of m-, p- and o-xylene; m-, p- and o-chlorotoluene; and m- and o-dichlorobenzene, although m- and p-xylene co-elute to the extent that their composite spectra is misinterpreted as the spectrum of a single compound. These compounds, as well as a number of other volatile organic compounds, have been detected at concentrations levels in the range of 200-600 ng per compound.

The practical detection limit for compounds in an unknown sample is the recognition of peaks in the Gram-Schmidt trace. In order to locate peaks not clearly observed in the Gram-Schmidt trace, a flame ionization detector has been used in tandem with the system's light pipe so that retention time for peaks can be determined on an initial run. The storage of spectra is then initiated manually based on these retention times, during a second analysis of the sample. Other, more appropriate, methods for data accumulation are being considered (see Recommendations).

Based on the current effort, the potential detection and identification limits are estimated at less than 100 ng per compound per cartridge, or ppb levels of detection for 20 L air samples drawn through TENAX-GC sorbent cartridges.

SECTION 3

RECOMMENDATIONS

Thermal desorption combined with GC/FTIR has been demonstrated to be effective in detecting and identifying volatile-organics in laboratory-generated mixtures, including the distinction between isomers, at the level of a few hundred nanograms per compound per cartridge. From the results obtained to this point, several additional improvements to the method which will (1) reduce the degree of operator intervention, (2) decrease analysis time and (3) significantly lower detection and identification limits can be recommended:

1. A user-generated library of spectra of target compounds should be established to supplement the Sadtler library. These spectra should be obtained using the complete desorption-GC/FTIR system, from authenticated mixtures loaded at the level of ca. 1000 ng per compound per cartridge.

2. Changes in the hardware and/or software should be developed which will use the FID to trigger the saving of interferograms, rather than using the Gram-Schmidt trace. This might be accomplished by splitting the effluent from the GC column ca. 100:1, with the smaller part going to the more sensitive FID, and adjusting the length of the transfer tubing to the FID and the light pipe so that a peak would reach the FID ca. one second before the same peak is detected in the light pipe. This would be in lieu of the use of the FID after the light pipe. Alternatively, the GC/FTIR software might be modified so that (even with sequential use of the FID) interferograms would only be saved during intervals corresponding to peaks in the FID trace. This might be accomplished by saving the interferograms continuously to files which would be automatically erased 10 seconds later unless a peak was detected by the FID. This second (software) modification would be more complex to implement but would utilize the full sensitivity of the FID with no degradation of the FTIR sensitivity.

With either of the modifications above the Gram-Schmidt trace would be used primarily as an indicator of the quality of performance of the instrument. For compounds present at 300-500 ng per cartridge or higher, Gram-Schmidt peaks will usually be observed; however, more lightly loaded compounds would be detected and identified by automatically working up the interferograms saved by

the FID trigger, even when no Gram-Schmidt peak is obvious. A program or protocol for saving background interferograms will also be required.

3. An objective protocol for raising the sensitivity of the peak-picking program of the library search should be developed. The results of such searches, in which strong noise peaks could be excluded, could be compared to those of the standard search in ambiguous cases in order to obtain more clues to identification.

Other possible improvements to the technique involving equipment modifications, such as stopped-flow methods, or lengthening or otherwise changing the geometry of the light pipe, can be envisioned, but are beyond the scope of the initial phases of this study reported here.

SECTION 4

EXPERIMENTAL

CHEMICALS

Samples were prepared by the Northrop Services Inc. (NSI) Volatile Organics Standards Laboratory. Neat compounds (5 to 10 μ L amounts) are injected into 2L static dilution bottles full of zero grade helium. The resulting gas mixtures are equilibrated for a minimum of one hour at 65°C. Syringe samples of the mixture are analyzed by capillary gas chromatograph and referenced to diffusion tube standards that are certified by time dependent weight loss. This establishes accurate concentration values (typically 500 ppmV/compound) for the dilution bottle mixture.

The sample format consists of Pyrex tubes (10 cm long, 1.5 cm o.d., and 1.2 cm i.d.) packed with 1.35 g of TENAX-GC and capped at both ends with glass wool. These cartridges are initially baked out at 270°C to remove any residual contamination and then attached to a zero grade helium purge system. Known volumes of the gas mixture (typically 50 to 100 mL) are injected into this purge stream, which serves to deposit the analytes onto the TENAX-GC. After being loaded, the sample cartridges are individually sealed in glass vials with Teflon-lined caps. A typical sample set of five to ten vials is placed in a container partially filled with activated charcoal and then stored in a freezer at the NSI facility until needed. Standard operating procedures and quality assurance information are available from NSI¹⁵.

INSTRUMENTATION

The analytical instrumentation incorporates three subsystems, each of which is commercially available. They are: 1) a Nutech model 320 cartridge desorption and sample injection system (Nutech Corp., Durham, NC), 2) a Varian 3700 gas chromatograph (Varian Associates Inc., Palo Alto, CA),

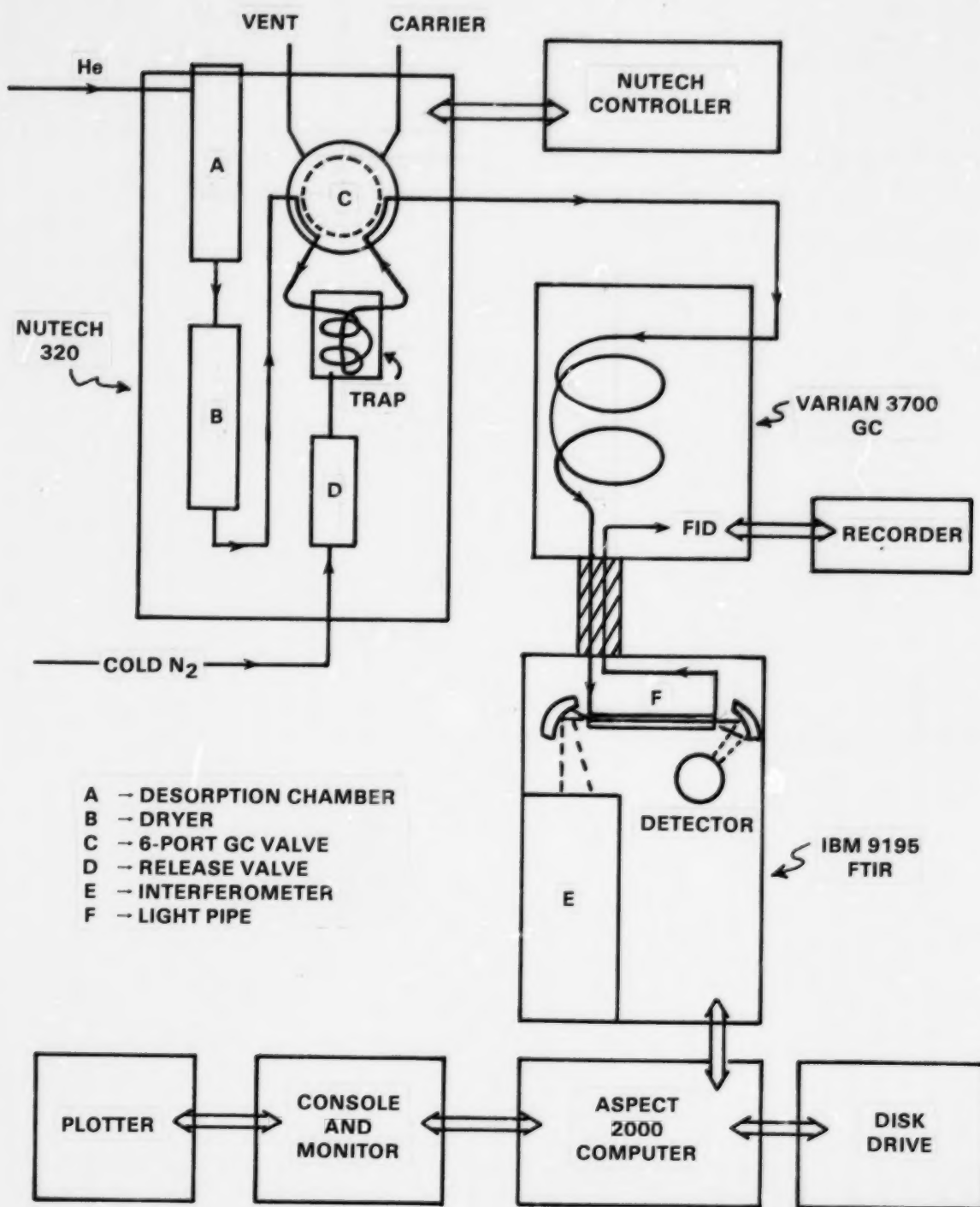


Figure 1. Block diagram of thermal desorption-GC/FTIR system.

and 3) an IBM model 9195 Fourier transform infrared spectrometer (IBM Instruments, Inc., Danbury, CT). These were interfaced for split-less on-column injection and subsequent serial infrared and flame ionization detection, using the IBM Model F2752 on-the-fly (light pipe) GC/FTIR interface attachment. A block diagram of the overall system is given in Figure 1.

Nutech desorption and sample injection unit. -- The Nutech unit consists of an electronics console for monitoring, setting and controlling temperatures, and a sample handling unit containing the cartridge desorption chamber, the cryogenic trap and the injection system. The gas flow arrangement for either cartridge desorption onto the cryotrap, or analyte injection from the trap to the column is selected manually by operating a six-port valve. A flow diagram for both valve positions is given in Figure 2.

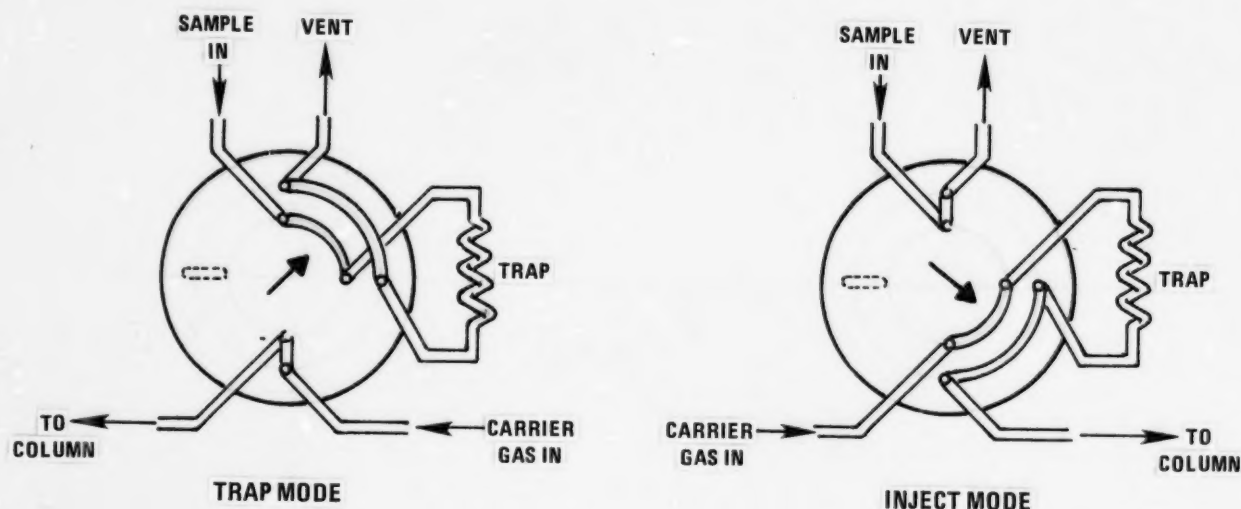


Figure 2. Flow diagram for six-port valve.

Independent temperature control channels in the electronics console can be set to automatically maintain the desorption chamber and valve block temperature, the cryotrap temperature (either at a low value during cartridge desorption or a high value during sample injection), and the external sample line temperature. Elevated temperatures are maintained by appropriate cycling of feedback controlled resistance heaters. The low cryotrap temperatures are maintained by feedback controlled flow of a nitrogen gas stream cooled by a liquid nitrogen bath. Trap temperature set points can be switched quickly from one to the other by the push of a button on the electronics console. All temperatures and temperature setpoints can be monitored on a digital display.

Perma-Pure dryer. -- In order to remove the traces of water adsorbed by and subsequently desorbed from the TENAX-GC, a special dryer (Perma-Pure Inc., MD-125-48(T)) is inserted after the Nutech desorption chamber and before the 6-port valve. The dryer is 48 in long and consists of two concentric tubes, the inner one (0.065 cm i.d., 0.12 cm o.d.), which carries the GC effluent, is made of Nafion and is permeable to water but virtually impermeable to the target organic compounds. The outer tube is made of Teflon (0.25 in i.d.). The annular space between the tubes is swept by a 250 mL/min flow of dry nitrogen. The dryer is wrapped with heating tape and is heated to 100°C between sample collections. This drives off residual water to increase the dryer's efficiency. Details of this procedure are given in reference 14.

Varian gas chromatograph. -- The Varian 3700 gas chromatograph features oven-temperature programming capability (-100°C to +300°C range) and is equipped with a flame ionization detector (FID). The standard injection port, inlet tubing, and carrier gas plumbing were bypassed to accommodate direct on-column injection from the Nutech sample transfer tubing. The connection from sample transfer tubing to the capillary column was placed outside of the GC oven so that re-trapping of injected sample (due to sub-ambient oven temperatures) would occur on the column head rather than on the transfer tubing. Column carrier flow (zero grade helium) was maintained at 2 mL/min by an externally mounted mass flow controller (FC-260, 0-10 mL/min He, Tylan Corp., Torrence, CA).

The column is a 30 m, 0.25 mm i.d. fused silica SE-54 WCOT (Model 475771, IBM Instruments). The oven temperature is programmed for 5 min at -50°C , then increased at a rate of $8^{\circ}/\text{min}$ to a maximum of 150°C , and then maintained at 150°C until all peaks have eluted. Sub-ambient oven temperatures are generated by released liquid nitrogen, controlled by the cryogenic accessory of the Varian 3700.

Fourier transform infrared spectrometer. -- The IBM 9195 employs a Genzel interferometer with a 7W globar source and germanium-on-KBr beamsplitter. Instrument control, data collection and storage, interferogram transformation (by Cooley-Tukey FFT with Happ-Genzel apodization), data manipulation, library storage and search and spectral printout are performed by the associated Aspect 2000 computer. The computer has a 16 Mbyte fixed disk and 16 Mbyte removable disk (CDC 9405) and is controlled through the instrument console keyboard and CRT monitor. The fixed disk contains the operating system, instrument control programs, Fourier transform algorithms and spectral library (Sadler IRVAP 8x16; 8000 spectra). Data collection and storage employs the removable disk, which can accommodate over 2500 individual interferograms at 8 cm^{-1} resolution.

For GC/FTIR operation the infrared beam is diverted into the GC interface unit. There it is focused into the 1.4 mm gold coated bore of the 36 cm long pyrex light pipe.¹⁷ The beam traverses the length of the light pipe undergoing multiple reflections, is collected at the other end and focused on a selected mercury cadmium telluride (MCT) detector ($D^* = 63 \times 10^9\text{ cm Hz W}^{-1}$, with a spectral range of $4000\text{--}800\text{ cm}^{-1}$).

Eluent from the GC column is conveyed to the light pipe by heated glass-lined stainless steel tubing and flows through the light pipe from source end to detector end. The flow rate is adjusted to ca. 32 cc/min so that a typical unsaturated peak will slightly overfill the light pipe bore and have a residence time in the light pipe of ca. 1 second. The effluent from the light pipe is returned to the FID of the GC where it generates a standard chromatogram with a delay time of ca. 4 second with respect to the FTIR response. The light pipe and glass-lined transfer lines are maintained at 150°C by automatic temperature controllers.

During GC/FTIR operation the FTIR is operated at mirror velocity 13 (0.559 cm/sec; optical velocity 2.237 cm/sec) and resolution 8 cm^{-1} . This allows 5 scans/second and thus 5 scans to be collected during the residence of a typical chromatographic peak in the light pipe. (Although two higher velocities are available, velocity 13 was found to give optimum performance. Higher resolution is, of course, also possible but would unacceptably reduce the scan repetition rate.) The data are collected using the Gram-Schmidt algorithm¹⁸. This algorithm computes a single point interferogram based on the average of the total absorption detected by each scan. These single points computed at the rate of 5 per second constitute a real-time FTIR-generated chromatogram (the Gram-Schmidt trace). When the automatic triggering mode is selected, interferograms are stored only if the value of the Gram-Schmidt trace point is above a preset threshold. Alternatively, interferogram storage can be manually triggered by the operator when a peak in the Gram-Schmidt trace is observed to begin on the CRT display. Subsequent to the GC/FTIR run the operator may designate those scans corresponding to specific peaks in the Gram-Schmidt trace which are to be co-added and transformed. The resulting spectra are divided by a carrier gas reference spectrum, converted to absorption files and then compared to the library, which is automatically searched to produce the 10 most likely hits based on peak matching. Prior to searching, the spectra may also be background corrected by subtracting the transformed sum of an equal number of interferograms collected from an adjacent peak-free portion of the Gram-Schmidt trace. Spectra may also be compared to user generated library files, e.g., of selected target compounds.

PROCEDURES

Data Collection

The procedure for performing GC/FTIR analyses on TENAX-GC cartridges was developed after extensive initial testing. Assuming that all instruments are turned on, the FID is lit and the FTIR detector is stabilized, other initial conditions are:

- 1) Nutech block and desorption chamber: 200°C
- 2) Nutech trap temperature: 120°C
"cool" mode set point: -150°C (not activated)
- 3) Nutech sample line temperature: 70°C
- 4) Nutech sample valve: inject position
- 5) GC oven temperature: 150°C
- 6) GC detector temperature: 150°C
- 7) Flow settings:
 - carrier: 2 mL/min
 - make-up helium: 30 mL/min
 - FID air: 450 mL/min
 - FID H₂: 30 mL/min
 - Cartridge desorption: 15 mL/min helium
- 8) GC oven temperature program
 - initial time: 5 min
 - initial temp.: +150°C
 - program rate: 8°C/min
 - final temp.: +150°C
 - final time: ∞ min

- 9) Chart recorder for FID zeroed and stable.

The sequence of operations is as follows:

1. Change Nutech trap temperature controller to "cool" mode; set point should be -150°C.
2. Set GC oven initial temp to +50°C.
3. Wait until Nutech trap temperature reads ca. -145°C (typically 15 min).
4. Open desorption chamber, insert sample cartridge and close chamber as rapidly as possible.
5. Switch Nutech valve to desorb position and start timer.
6. Set GC oven initial temperature to -50°C.
7. When timer reads ca. 20 min., check FTIR baseline and if necessary fine tune optics.

8. When timer reads 30 min, start FTIR-GC program and, upon hearing three signal tones, do the following in sequence:
 - 1) Turn valve to inject position.
 - 2) Change Nutech trap to temperature "heat" mode.
 - 3) Begin GC oven temperature program.
9. Activate FTIR interferogram collection mode at appropriate times (if in manual trigger mode).
10. When all peaks have eluted, stop FTIR.
11. Set GC oven initial temperature to +150°C and stop GC oven temperature program.
12. Open desorption chamber: remove cartridge. Close desorption chamber.
13. Perform any appropriate data post-processing, spectra plotting, etc., as per IBM 9195 Operating Manual.

SECTION 5

RESULTS

1. System evaluation: preliminary data and efforts to solve water interference problems.--In order to evaluate the combined systems, preliminary separation and spectral determinations were made using relatively concentrated gas mixtures injected directly into the helium purge line of the Nutech desorption unit. These initial tests involved sample mixtures of compounds such as that listed in Table 1. This mixture was prepared in a 6 L stainless steel canister by first evacuating the canister to 2×10^{-2} torr, then back-filling with 2.5% H_2O in N_2 to atmospheric pressure and then pressurizing to 30 psi gauge with dry N_2 containing 10 ppmV of each of the compounds in Table 1. The resulting gas was thus ca. 6 ppm in each component of interest and ca. 8000 ppm H_2O . Humidified air was used because of the likely interference of H_2O with IR detection and the inevitability of water contamination of samples collected from ambient air.

This gas mixture was then metered (using the mass flow controller) into the helium purge line of the Nutech desorption unit at a rate of 10 mL/min for 10 min while maintaining the Nutech trap at $-150^\circ C$. The 100 mL sample trapped in this manner contained from 1500 to 2000 ng of each of the organic components. Subsequent following of the standard procedures as outlined in the Experimental Section produced the FID and real-time FTIR (Gram-Schmidt) chromatograms in Figures 3-5. Two analysis runs were made, first without the Perma-Pure dryer and then after insertion of the dryer. In either case the FID chromatogram (Figure 3) is essentially the same except for small differences in retention times and does not reflect the presence of H_2O . However, the FTIR Gram-Schmidt trace shows dramatically the interference of H_2O with IR detection. Without the dryer (Figure 4), the broad double maximum band from the H_2O extends from 13-18 minutes and virtually masks peak 9. After insertion of the dryer (Figure 5), the water band extends only from 13 and 15 minutes. The presence of water vapor at these target gas concentrations does not appear serious, even in the sample

TABLE 1
INITIAL TEST GAS MIXTURE

<u>Compound</u>	<u>FID Peak No.</u> <u>(Figure 3)</u>	<u>FTIR-MCT Peak No.</u> <u>(Figures 4 and 5)</u>
propane	1	1
vinyl chloride	2	2
vinylidene chloride	3	3
trichlorotrifluoroethane	4	4
chloroform	5	5
1,2-dichloroethane	6	6
1,1,1-trichloroethane	7	-
carbon tetrachloride	8	7
trichloroethylene	9	8
(cis)1,3-dichloropropane	10	9
(trans)1,3-dichloropropane	11	10
1,2-dibromomethane	12	11
tetrachloroethylene	13	
chlorobenzene	14	12
benzylchloride	15	13
1,3-hexachlorobutadiene	16	14

run without the dryer. However, at the few hundreds of nanograms level, as shown below, the removal of as much water as possible is highly desirable.

A representative spectrum of one of the compounds in this initial mixture (peak 9, trichloroethylene) as calculated from the co-addition of the interferograms stored during the interval of the passage of the compound through the light pipe (interval of Gram-Schmidt peak) is shown in Figures 6 and 7. Comparing Figure 6 to Figure 7, we note the difference in quality of the calculated spectrum without (Figure 6) and with (Figure 7) the Perma-Pure dryer. The strong background in Figure 6 is clearly due to H₂O. In fact, when the spectrum in Figure 6 was subjected to the peak picking program of

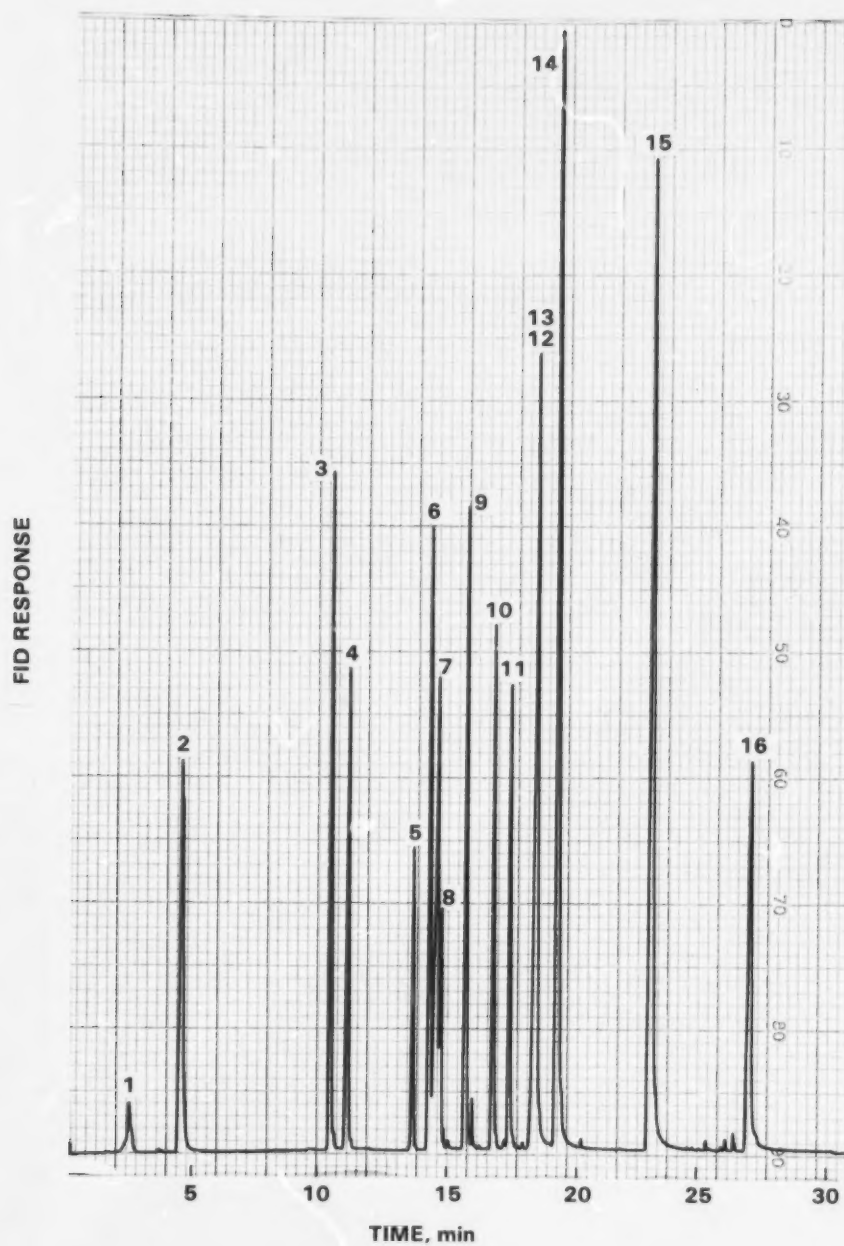


Figure 3. Post-light pipe FID trace for GC analysis of mixture of compounds in Table 1 obtained without use of Perma-Pure dryer.

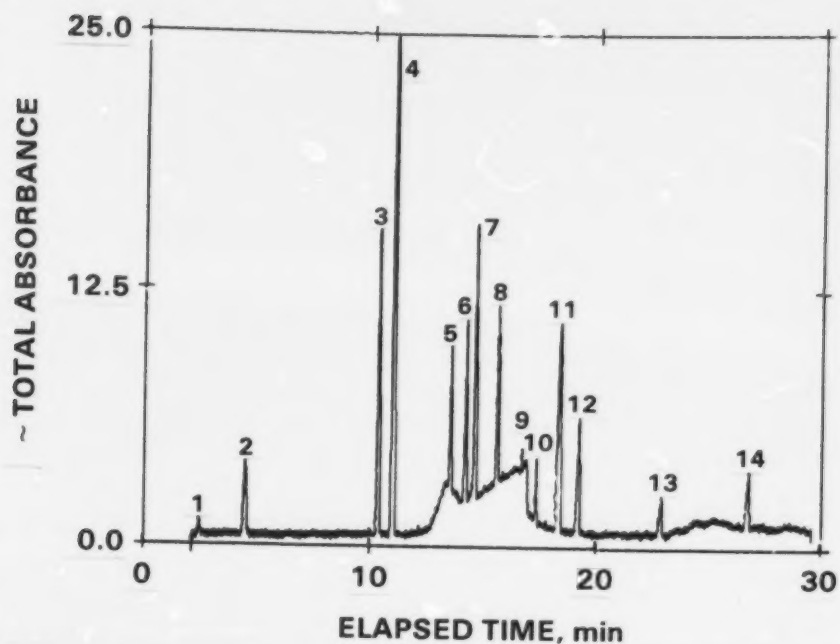


Figure 4. GC/FTIR Gram-Schmidt trace for analysis of mixture of compounds in Table 1 obtained without use of Perma-Pure dryer.

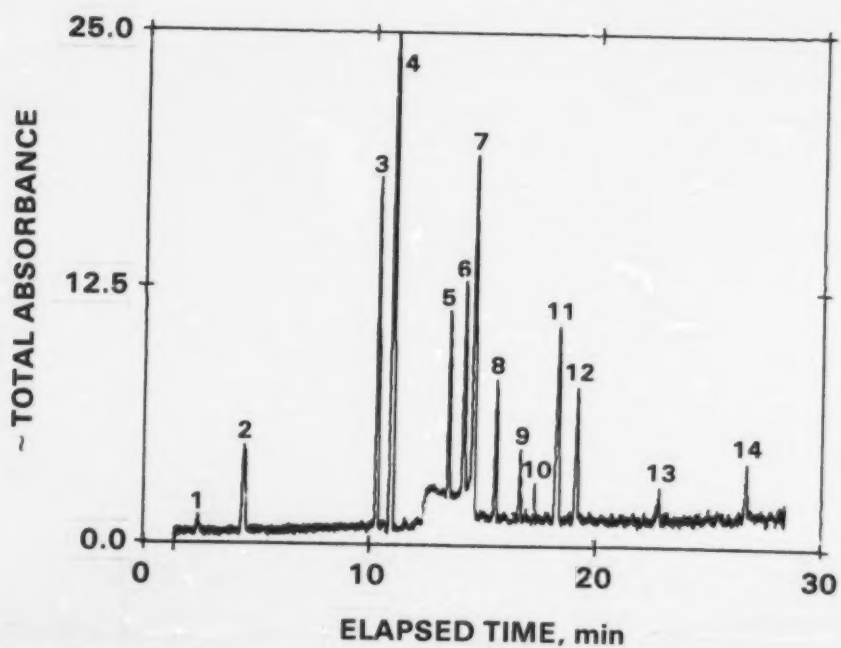


Figure 5. GC/FTIR Gram-Schmidt trace for analysis of mixture of compounds in Table 1 obtained with use of Perma-Pure dryer.

the spectral search routine, a water peak (1458 cm^{-1}) was picked over one of those of trichloroethylene (1250 cm^{-1}). With the dryer the 1250 cm^{-1} peak is identified. As will be shown below, subtraction techniques can be applied to extract spectral information even more clearly, but the removal from the sample of as much water as possible, is obviously desirable.

2. Initial evaluation of TENAX-GC desorption of samples.-- An initial series of tests of the desorption methodology was performed by the procedures outlined in the Experimental Section. The composition of one of these samples in terms of weights loaded on the cartridge (as determined by NSI) is given in Table 2. The FID and Gram-Schmidt chromatograms of two of these samples desorbed from (ostensibly identically loaded) TENAX-GC cartridges, are shown in Figures 8 to 10. Nine of the 14 constituent compounds are identified by their retention times in the FID chromatogram (Figure 8) (by comparison to the NSI chromatographic data supplied with the samples). The correlation of the other five compounds with the remaining 5 peaks in the FID trace is uncertain. No water peak is observed in the FID data either with or without the dryer. The Gram-Schmidt trace without (Figure 9) and with (Figure 10) the Perma-Pure dryer again shows the H_2O interference in IR detection and the effectiveness of the dryer in reducing the water level. (In these data the weakness of the CCl_4 chromatographic peaks is thought to be due to loss of CCl_4 from the cartridge prior to its analysis. CCl_4 is known to have a substantial vapor pressure on TENAX-GC.)

Although the data illustrated in Figures 9 and 10 were obtained in the course of evaluation of the Perma-Pure dryer and do not represent quality of results obtained at the current stage of development, a work up of one of the peaks in the Gram-Schmidt chromatogram is illustrative of the problems and potentials of the method.

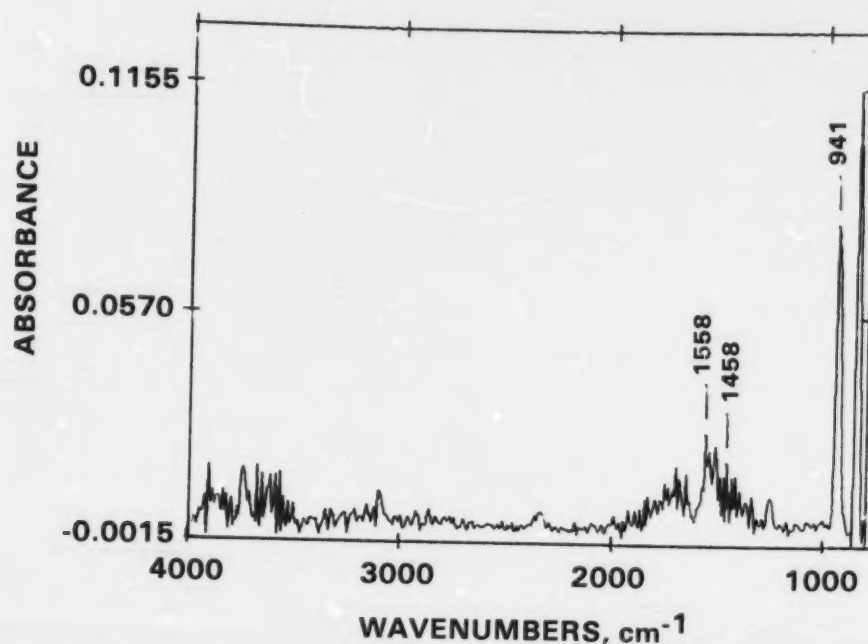


Figure 6. Absorption spectrum generated from transformation of interferograms collected during passage through the light pipe of peak 9 in Figure 4 (without dryer).

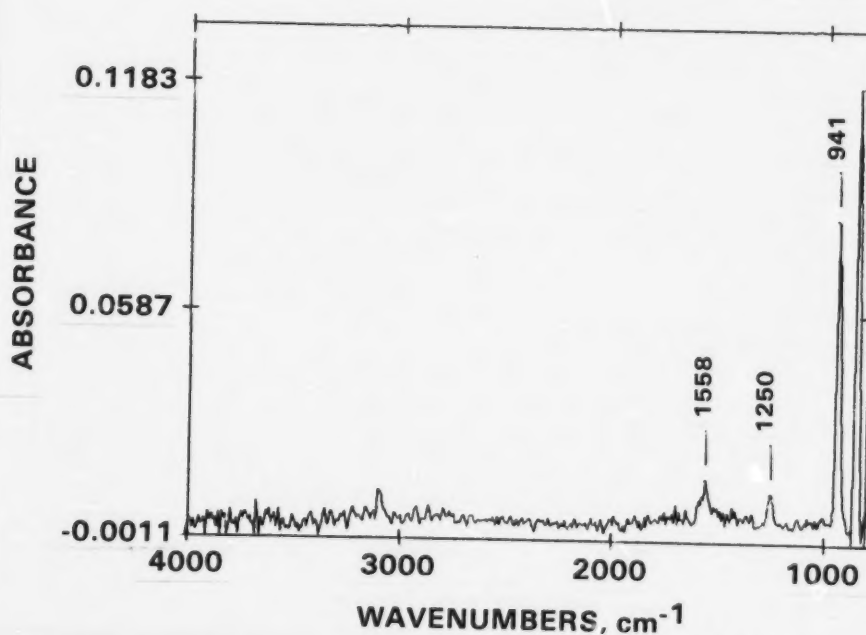


Figure 7. Absorption spectrum generated from transformation of interferograms collected during passage through the light pipe of peak 9 in Figure 5 (with dryer). Identified as trichloroethylene by library search.

TABLE 2.
TENAX-GC DESORPTION EVALUATION MIXTURE

<u>Compound</u>	<u>Loading (ng)</u>	<u>FID Peak No.</u> <u>(Figure 8)</u>	<u>FTIR Peak No.</u> <u>(Figures 9 and 10)</u>
chloroform	397	1	1
1,2-dichloroethane	338	2	2
methylchloroform	358	3	3
benzene	236	4	4
carbon tetrachloride	428	5	5 ^a
b		6	6
trichloroethylene	392	7	7
toluene	233	8	8
b		9	9
chlorobenzene	297	10	10
b		11	
b		12	
b		13	
o-xylene	236	14	
1,2-dichloropropane	310	b	
tetrachloroethylene	425		
ethylbenzene	233		
1-bromo-3-chloropropane	428		
bromoform	464		

^a Positive identification demonstrated in Figure 13.

^b Peaks 6, 9, 11, 12 and 13 are ascribed to the five compounds listed but were not further identified.

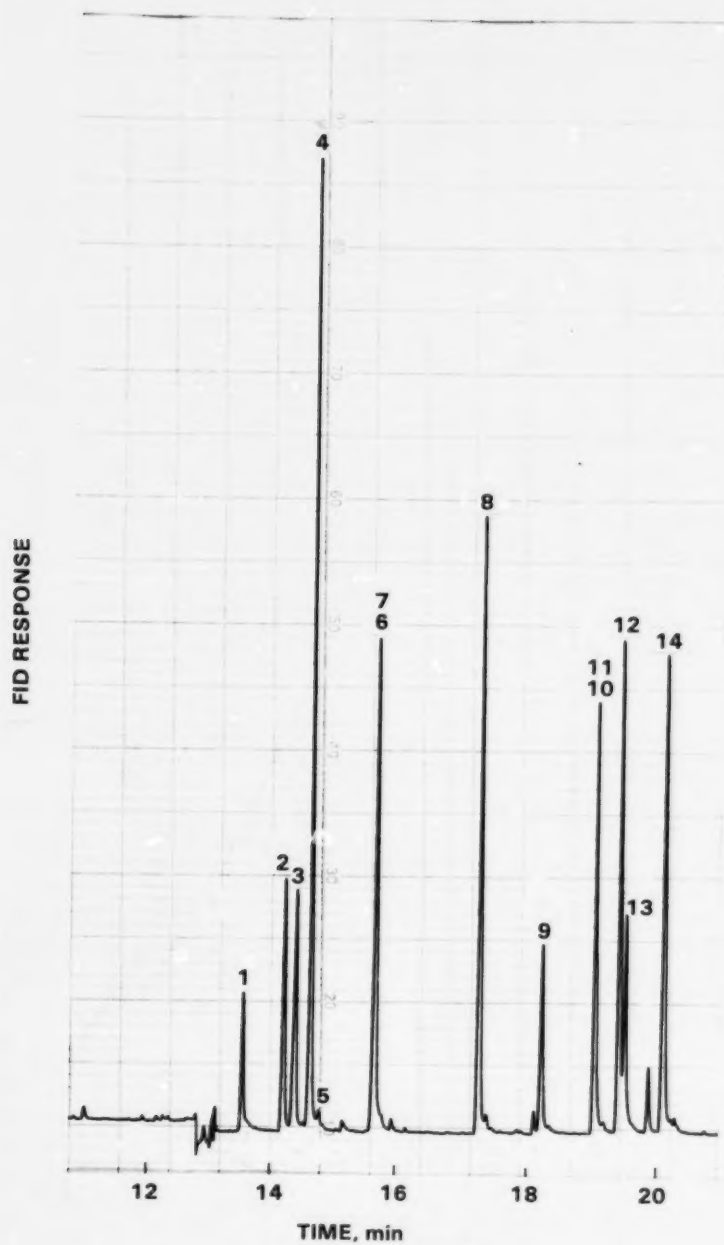


Figure 8. Post-light pipe FID trace for GC analysis of compound mixture in Table 2 as desorbed from TENAX-GC without Perma-Pure dryer.

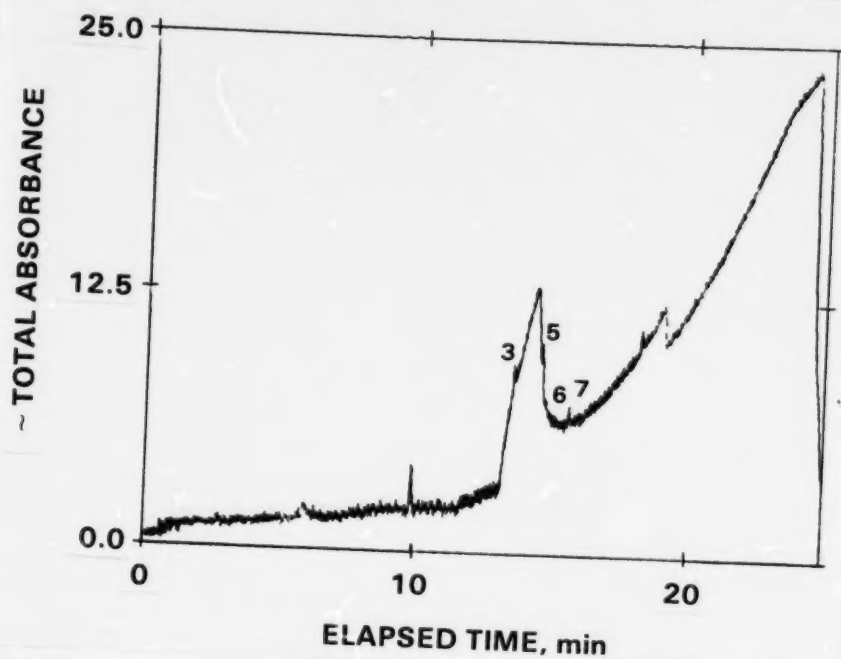


Figure 9. GC/FTIR Gram-Schmidt trace for analysis of compound mixture in Table 2 desorbed from TENAX-GC without Perma-Pure dryer.

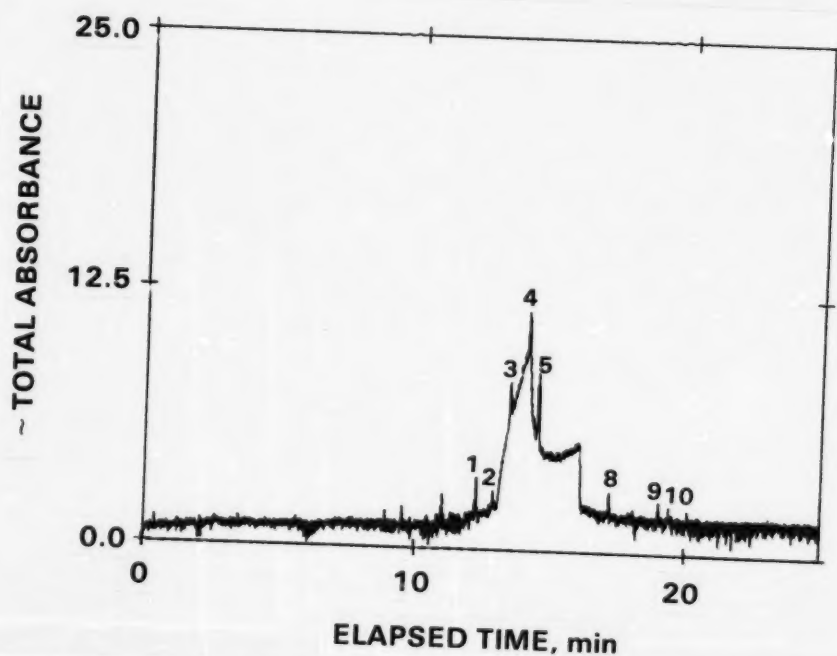


Figure 10. GC/FTIR Gram-Schmidt trace for analysis of compound mixture in Table 2 as desorbed from TENAX/GC with Perma-Pure dryer in place.

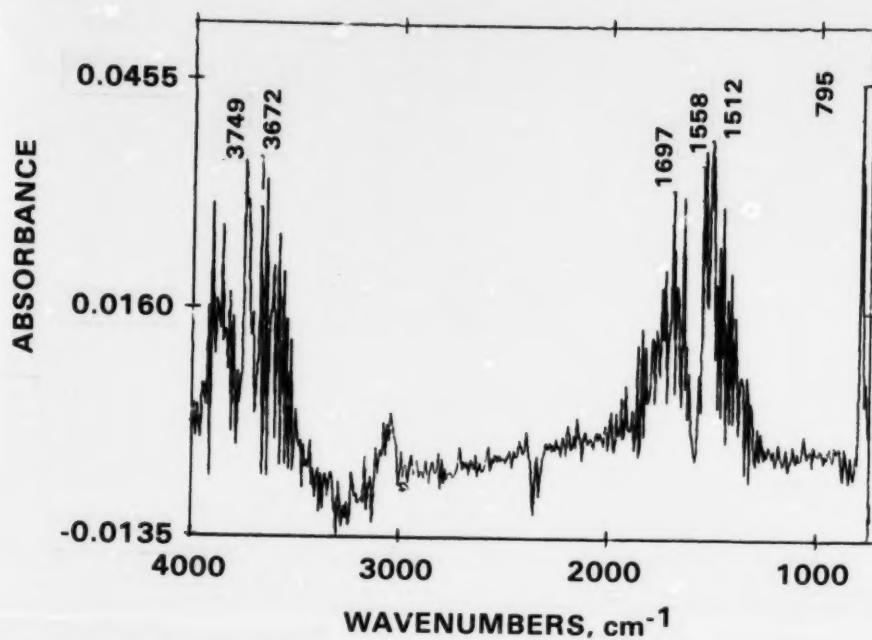


Figure 11. Absorption spectrum generated from transformation of interferograms collected for peak 5 in Figure 9 (without dryer or background correction).

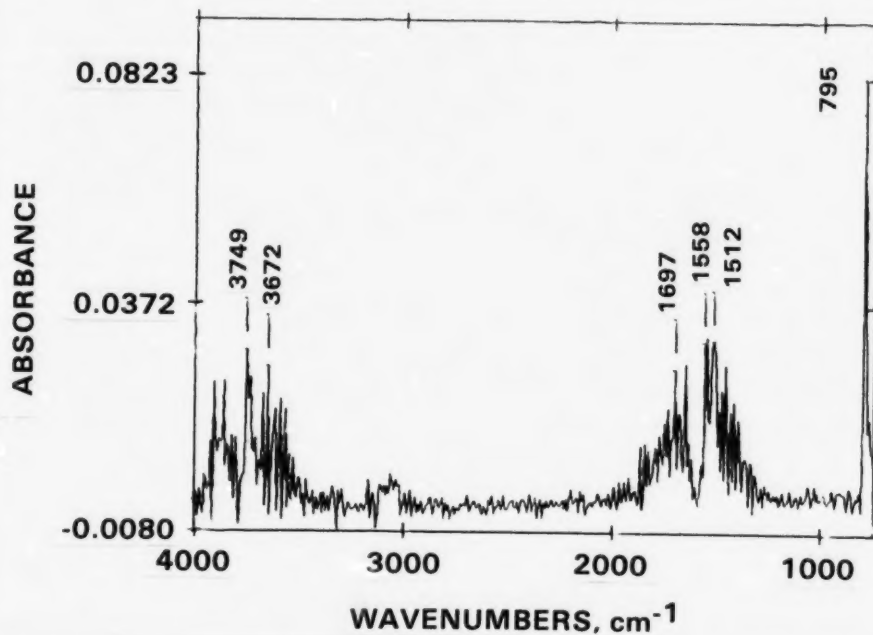


Figure 12. Absorption spectrum generated from transformation of interferograms collected from peak 5 in Figure 10 (with Perma-Pure dryer).

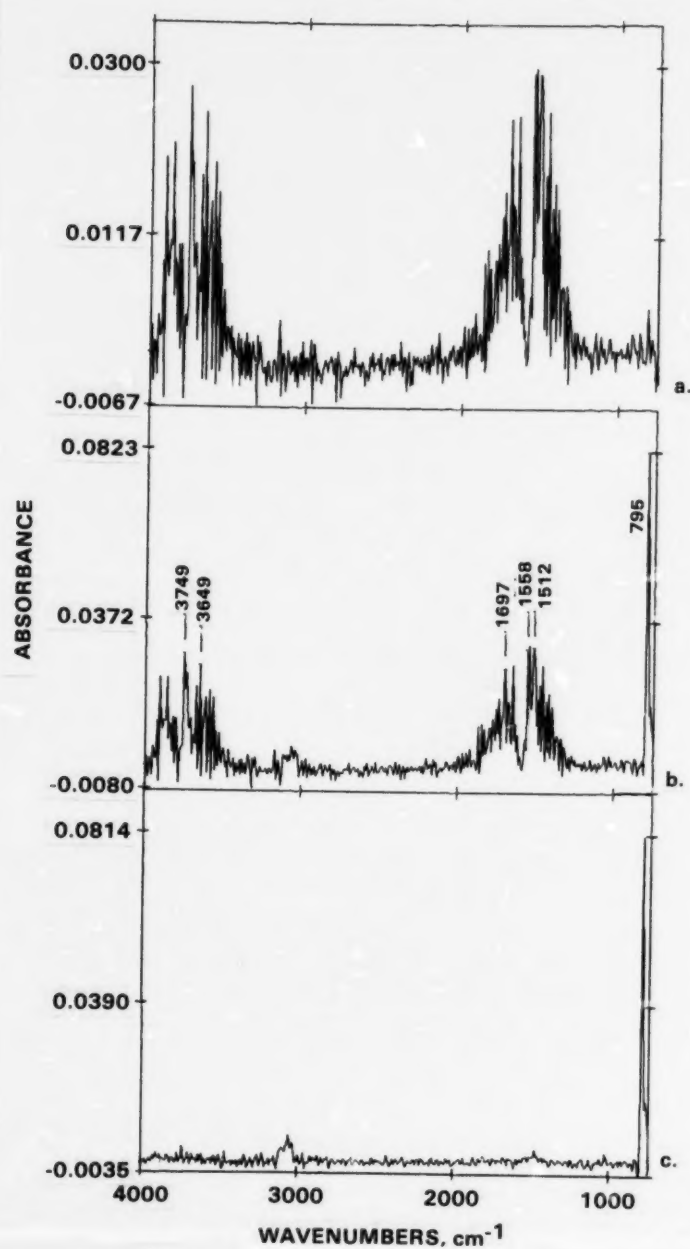


Figure 13. Illustration of efficacy of background correction.
 a. Background absorption generated from transformation of interferograms collected adjacent to peak 5 in Figure 10.
 b. Same as Figure 12 (peak 5, Figure 10)
 c. Backgrounded corrected spectrum of peak 5, Figure 10 (b-a).

Barely visible in Figure 9, but clearly visible in Figure 10, at ca. 14.5 min is a peak in the Gram-Schmidt trace which corresponds either to peak 4 or 5 in the FID trace (Figure 8). Figure 11 shows the absorbance file from the transform of the co-added interferograms collected for this peak from the run without dryer (Figure 9) and Figure 12 shows the same result from the run with the dryer. The reduced importance of the water interference is obvious in Figure 12 relative to the single other IR band at 795 cm^{-1} . However, in either case, most of the peaks identified in the spectrum by the peak picking program appear to be those of water. Further treatment of the spectrum in Figure 12 by background subtraction is illustrated in Figure 13. In the resulting corrected spectrum (13c) only the peak at 795 cm^{-1} appears, clearly identifying the compound as CCl_4 and not C_6H_6 (i.e., peak 5 and not peak 4 in the FID trace). Apparently the weaker bands of CCl_4 from 1100 cm^{-1} to 1600 cm^{-1} are victims of the water bands in this region. The baseline subtracted in this case is the transform of interferograms collected just prior to the appearance of the Gram-Schmidt peak at 14.5 min.

3. Evaluation of complete system at current level of development:
identification of isomeric compounds in mixtures using the Sadtler library search.--The completed system was evaluated after the preliminary tests and evaluations of the equipment and procedures. A sample mixture of several sets of geometrical isomers of target compounds loaded on TENAX-GC cartridges was used for this evaluation. The composition and loading of these samples on the cartridges as determined by NSI are given in Table 3.

The FID and Gram-Schmidt chromatograms (with the Perma-Pure dryer in place) are shown in Figures 14 and 15, respectively. Note that all of these compounds elute after the broad water "band". An expanded view of the 18-24 minute portion of the Gram-Schmidt trace is shown in Figure 16.

TABLE 3.
GEOMETRICAL ISOMER DISCRIMINATION MIXTURE

<u>Compound</u> No.	<u>Loading (ng)</u>	FID Peak No. <u>(Figure 14)</u>	GC/FTIR Peak <u>(Figure 15)</u>
m-xylene	381	} 1	} 1
p-xylene	380		
o-xylene	389	2	2
o-chlorotoluene	477	3	3
m-chlorotoluene	473	4	4
p-chlorotoluene	471	5	5
m-dichlorobenzene	567	6	6
o-dichlorobenzene	575	7	7

The results of transformation of co-added interferograms collected during the passage of each of peaks 1-7 through the light pipe are shown in Figures 17 through 23. Each figure shows (a) the spectrum of the adjacent background, (b) the raw spectrum and, (c) the background corrected spectrum. The spectral search results, using the Sadtler IRVAP 8x16 library and associated search program, are given in Tables 4-10. (It should be noted that the automatic scale expansion feature of the plotting program gives different absorbance scales for parts (a), (b) and (c) of Figures 17-23. The intensity of the background correction was adjusted so as to give a flat base line with no negative excursions.)

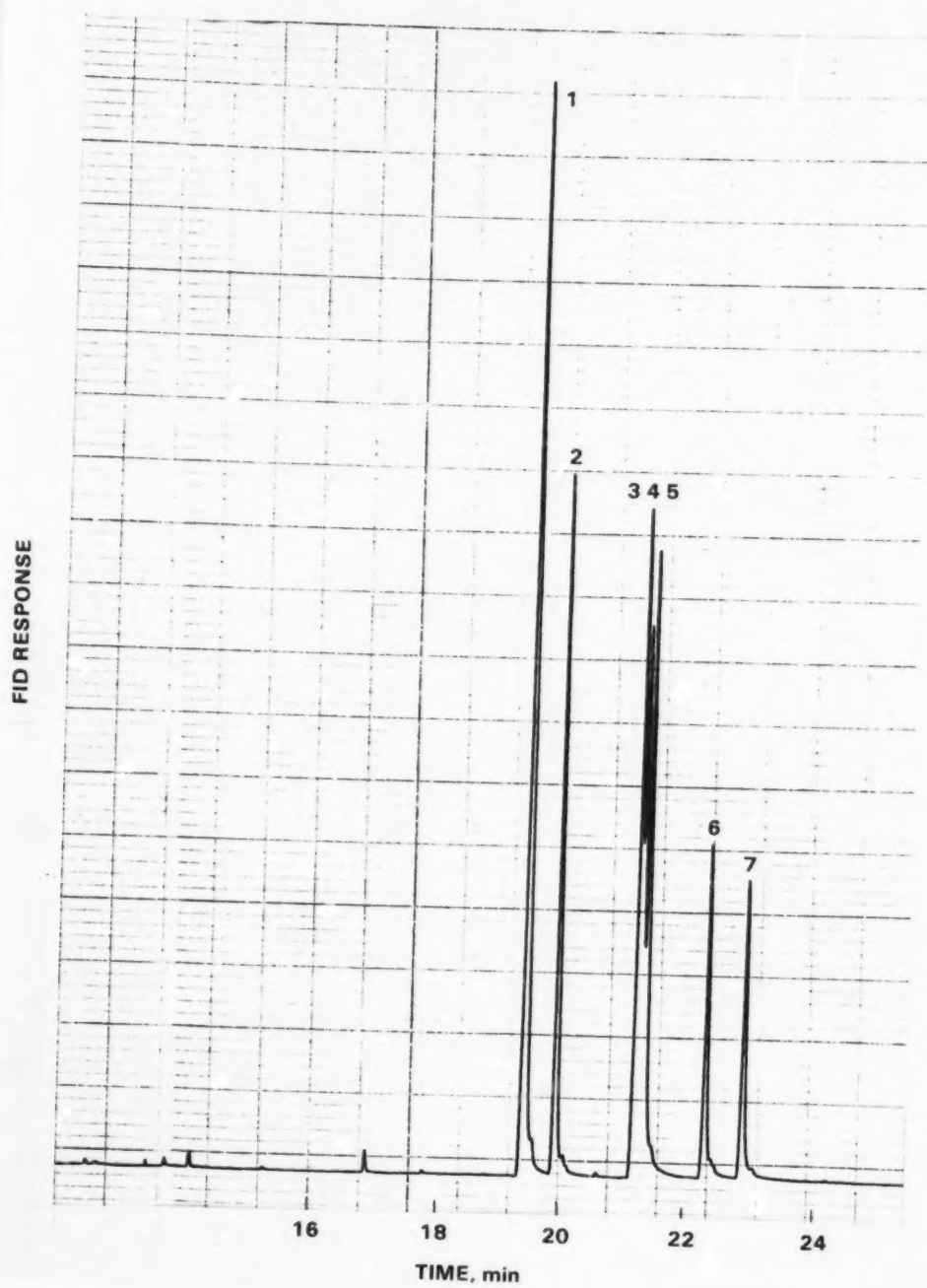


Figure 14. Post-light pipe FID trace for analysis of mixture of sets of isomers in Table 3.

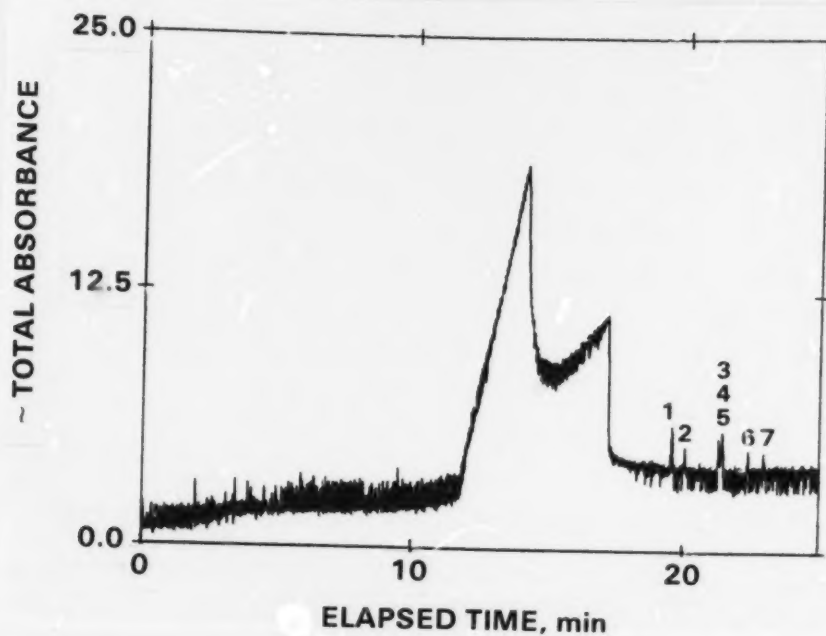


Figure 15. GC/FTIR Gram-Schmidt trace for analysis of mixture of sets of isomers in Table 3.

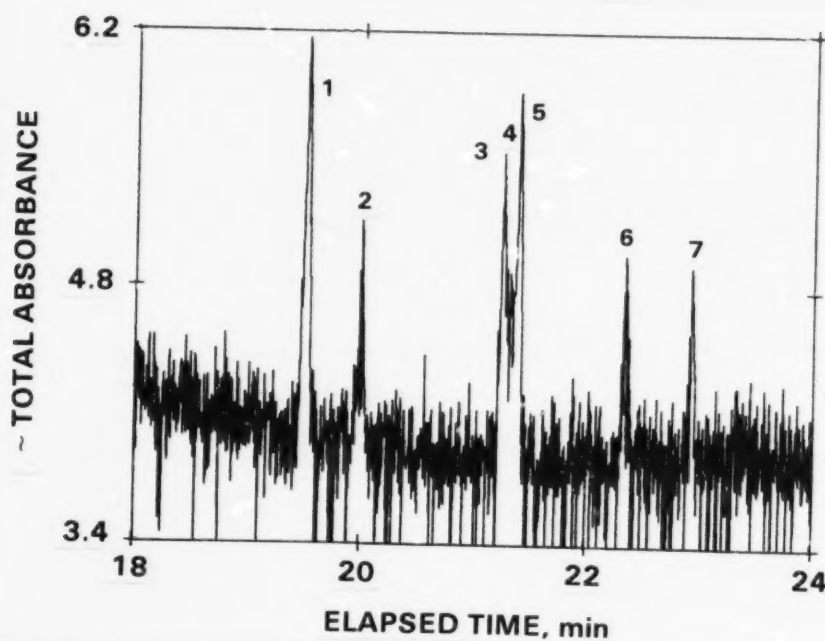


Figure 16. Expansion of the 18-24 minute portion of the Gram-Schmidt trace in Figure 15.

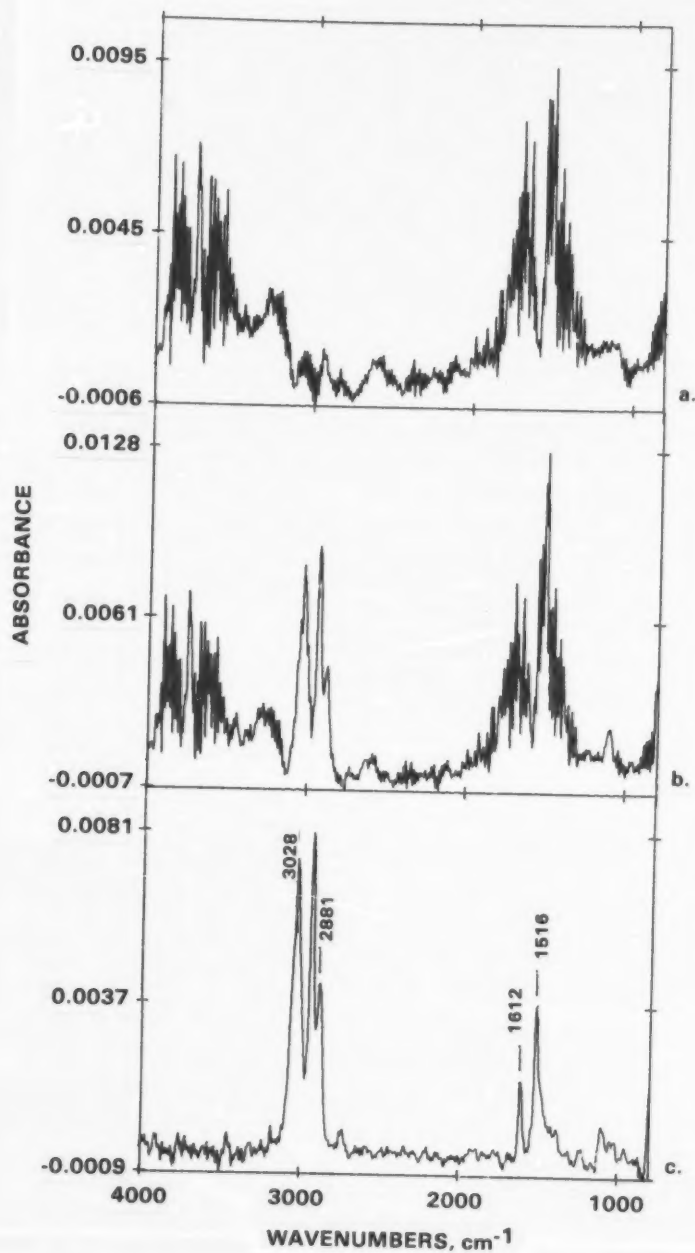


Figure 17. Peak 1, Figure 16 (m- and p-xylene)

- a. Absorption spectrum generated from baseline adjacent to peak interval (background correction)
- b. Uncorrected spectrum from peak interval.
- c. Corrected spectrum with peaks used for search identified (b-a)

TABLE 4

SADTLER IRVAP 8 x 16 LIBRARY SEARCH
 REPORT USING CORRECTED SPECTRA
 (M- and P-XYLENE), PEAK 1, FIGURE 16.

4 Peaks

Sensitivity: 20

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	1515.967	45	31
2	1612.402	20	23
3	2935.498	100	116
4	3028.076	91	69

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	714	7251	benzene,/1-cyclohexen-1-yl/-,
2	700	1877	4-hexadiene
3	628	2764	cyclopropanecarbonitrile,1-p-tolyl-,
4	620	5863	bibenzyl,4,4pr-dimethyl-,
5	616	4227	cyclooctene
6	610	6189	benzenetriamine,1,2,4-,N 1-phenyl-,
7	548	2211	4-xylidine
8	536	3498	mercury,diethyl-,
9	522	2044	piperidine,4-methyl-,
10	498	5348	aniline,2,4,5-trimethyl-,

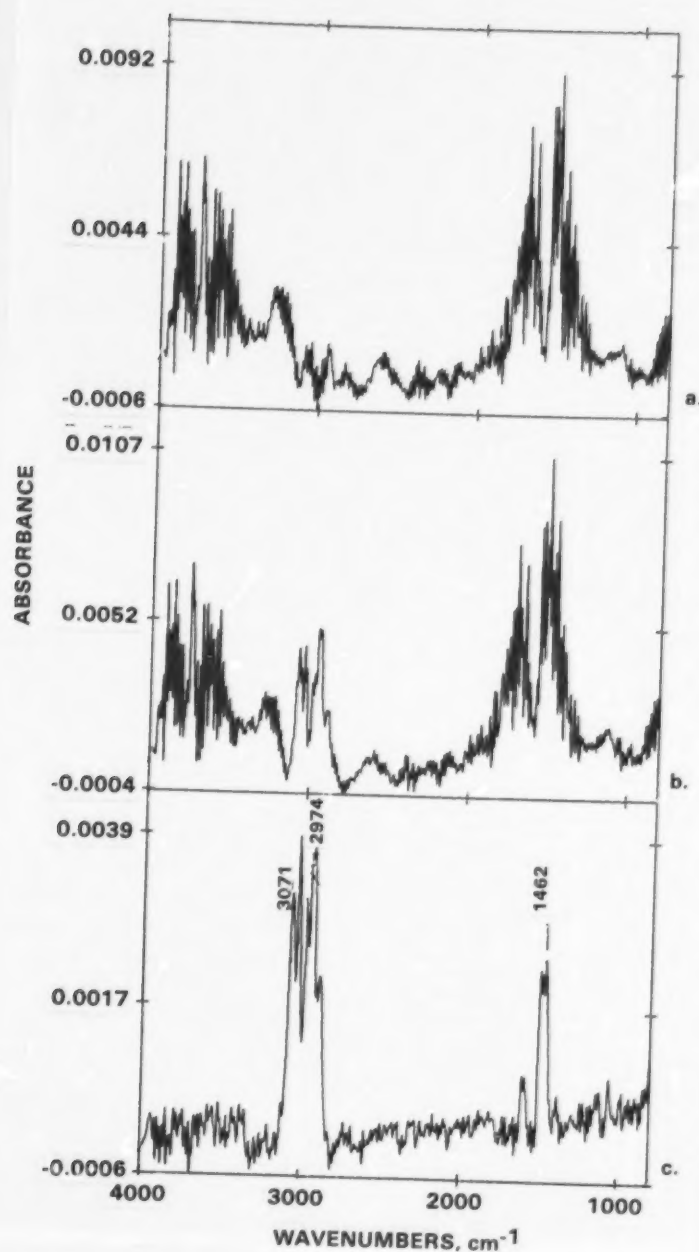


Figure 18. Peak 2, Figure 16 (o-xylene)

- a. Absorption spectrum generated from baseline adjacent to peak interval (background correction).
- b. Uncorrected spectrum from peak interval.
- c. Corrected spectrum with peaks used for search identified.

TABLE 5

SADTLER SEARCH REPORT
PEAK 2, FIGURE 16 (O-XYLENE)

20 Peaks

Sensitivity: 60

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	975.928	16	23
2	1056.934	21	19
3	1118.652	17	19
4	1461.963	60	31
5	1496.680	57	31
6	1608.545	21	15
7	2935.498	96	81
8	2974.072	74	23
9	3031.934	100	23
10	3070.508	80	31

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	434	6512	methane,fluoro-,
2	342	7591	2-butyne
3	308	728	3-hexanone,4-/2,4-dimethoxyphenyl/-,
4	298	4649	phenalen-1-one,2,3-dihydro-2,5,8-trimethyl-,
5	292	287	1-propanol,3-/o-toluino/-,
6	288	6955	methylmercaptan
7	286	4480	ketone,morpholino2-phenyl-1-cyclopropyl,trans-,
8	274	1617	2-picoline
9	272	1953	p-cymenol
10	262	1579	o-xylene

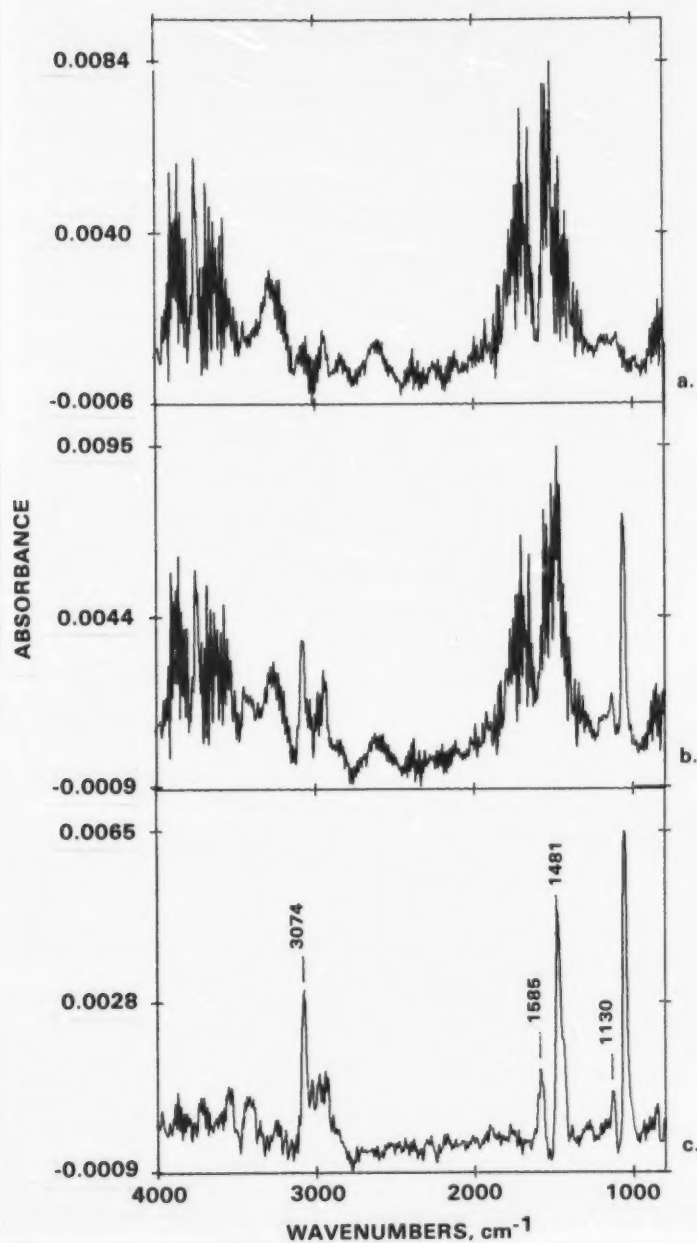


Figure 19. Peak 3, Figure 16 (o-chlorotoluene)

- a. Absorption spectrum generated from baseline adjacent to peak interval (background correction).
- b. Uncorrected spectrum from peak interval.
- c. Corrected spectrum with peaks used for search identified.

TABLE 6

SADTLER SEARCH REPORT
 PEAK 3, FIGURE 16 (O-CHLOROTOLUENE)

5 Peaks

Sensitivity: 40

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	1060.791	100	15
2	1130.225	13	23
3	1481.250	73	23
4	1585.400	20	46
5	3074.365	47	39

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	500	2792	acetophenone,2-,4-,6-trimethoxy-,
2	454	1617	2-picoline
3	442	7308	aniline,n-/p-methylbenzylidene/-,
4	440	6486	aniline,3,5-dimethoxy-,
5	402	3709	toluene,2,6-dimethoxy-,
6	384	4662	ethanol,2-ethoxy-,
7	380	1036	toluene,o-chlopo-,
8	378	5075	pyridazine,3-chloro-6-/isopropyl-
9	368	3406	amino/-,
10	366	3265	acetonitrile,methoxy-,
			o-anisonitrile,6-chloro-,

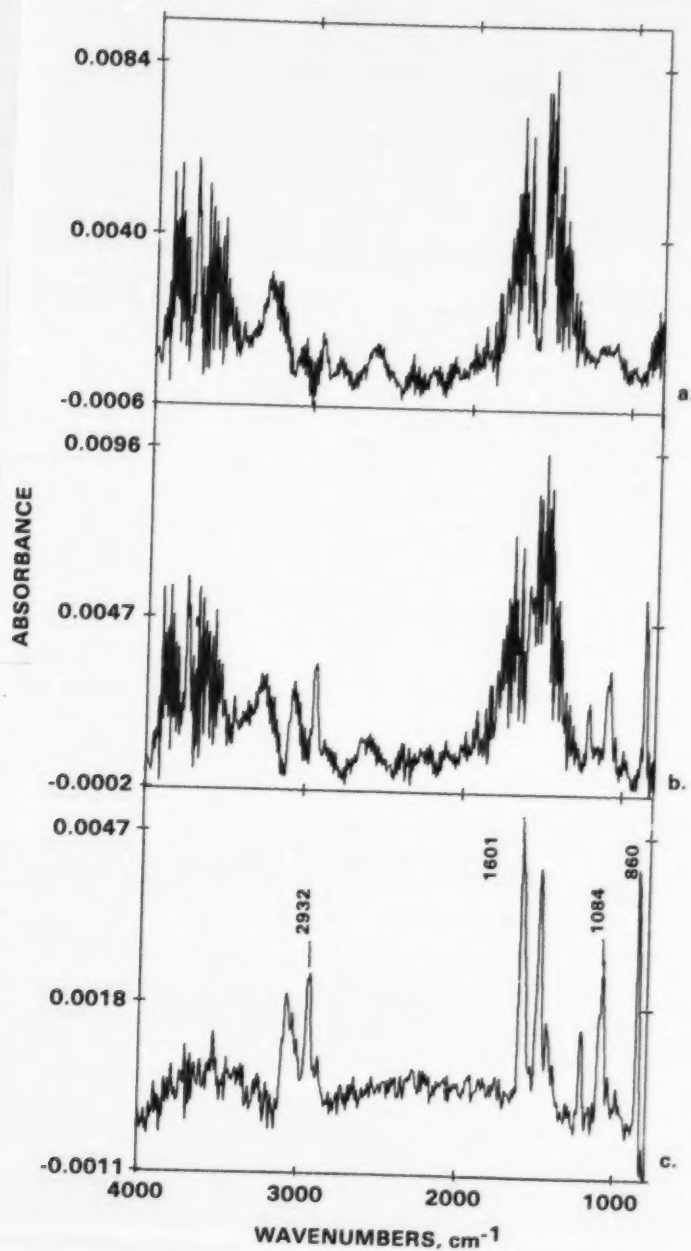


Figure 20. Peak 4, Figure 16 (m-chlorotoluene)
 a. Absorption spectrum generated from baseline adjacent to peak interval (background correction).
 b. Uncorrected spectrum from peak interval.
 c. Corrected spectrum with peaks used for search identified.

TABLE 7

SADTLER SEARCH REPORT
PEAK 4, FIGURE 16 (M-CHLOROTOLUENE)

15 Peaks

Sensitivity: 80

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	860.205	87	23
2	1083.936	56	46
3	1215.088	30	23
4	1392.529	18	15
5	1438.818	33	23
6	1481.250	89	27
7	1600.830	100	39
8	2283.594	15	93
9	2931.641	48	39
10	3074.365	41	54

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	444	1654	toluene,m-chloro-,
2	356	32	m-toluenethiol
3	278	4584	carbonmonoxide
4	266	2843	pyridine,2-pentyl-,
5	246	2822	toluene,m-bromo-,
6	218	5143	o-xylene,4-bromo-,
7	216	7144	azulene,4,6,8-trimethyl-,
8	212	7251	benzene,/1-cyclohexen-1-yl/-,
9	208	7995	2-pentyne
10	204	452	diphenylamine,2,2pr-di-sec-butyl-,

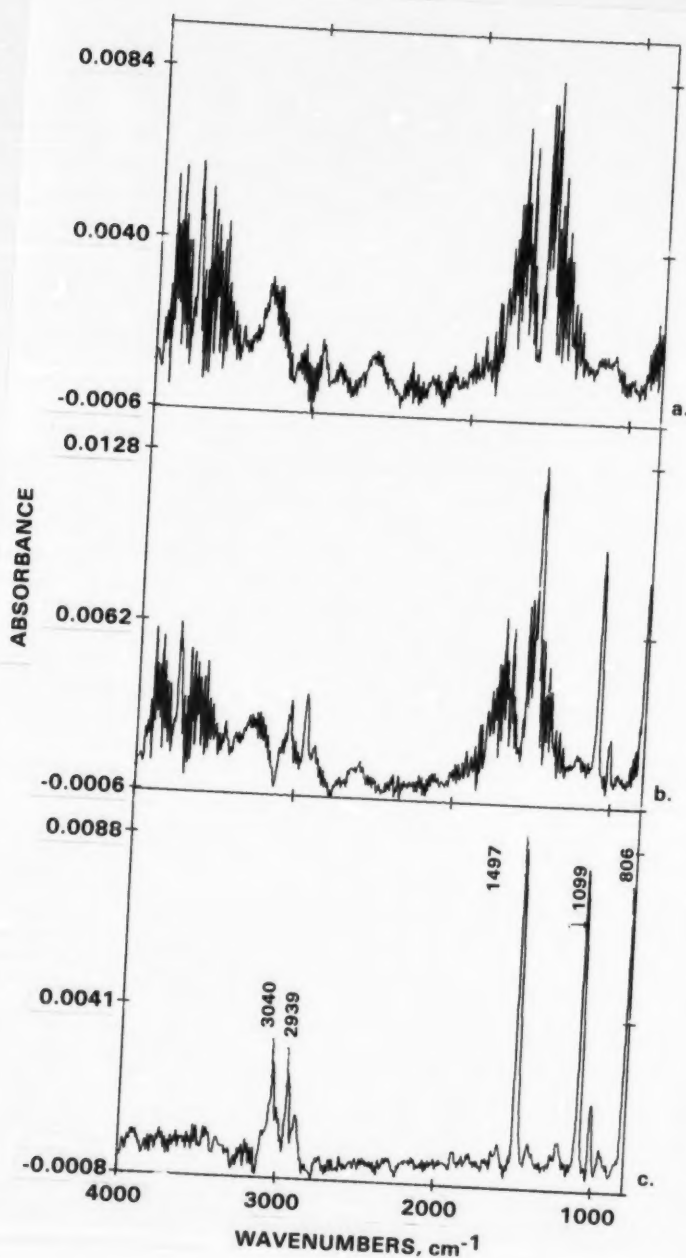


Figure 21. Peak 5, Figure 16 (p-chlorotoluene)
 a. Absorption spectrum generated from baseline adjacent to peak interval (background correction).
 b. Uncorrected spectrum from peak interval.
 c. Corrected spectrum with peaks used for search identified.

TABLE 8

SADTLER SEARCH REPORT
PEAK 5, FIGURE 16 (P-CHLOROTOLUENE)

6 Peaks

Sensitivity: 40

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	806.201	82	23
2	1018.359	19	23
3	1099.365	94	15
4	1496.680	100	23
5	2939.355	25	15
6	3039.648	28	46

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	676	5473	p-tolyldisulfide
2	658	68	toluene,p-chloro-,
3	604	4604	methane,bis/p-chlorophenyl/-,
4	584	6810	phenethylamine,p-chloro-,
5	560	2494	phenethylalcohol,p-chloro-,
6	558	2702	toluene,p-bromo-,
7	546	4631	benzylalcohol,p-chloro-,
8	526	1391	ether,p-chloro-a-/2-chloroethyl/- benzylmethyl,
9	494	7525	acrylonitrile,3-/p-chlorophenyl/-2-p- tolyl-,
10	468	3792	cyclohexanol,1-/p-chlorophenyl/-,

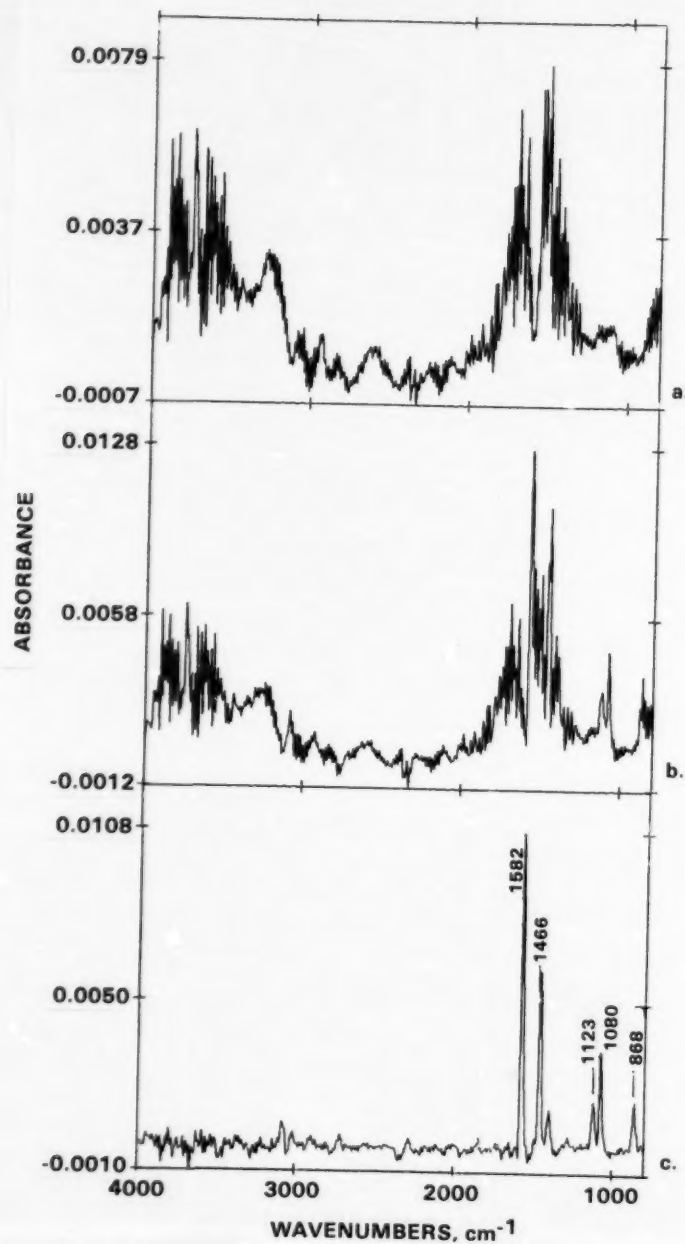


Figure 22. Peak 6, Figure 16 (m-dichlorobenzene)
 a. Absorption spectrum generated from baseline adjacent to peak interval (background correction).
 b. Uncorrected spectrum from peak interval.
 c. Corrected spectrum with peaks used for search identified.

TABLE 9

SADTLER SEARCH REPORT
PEAK 6, FIGURE 16 (M-DICHLOROBENZENE)

6 Peaks

Sensitivity: 80

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	867.920	14	23
2	1080.078	30	23
3	1122.510	14	31
4	1407.959	12	31
5	1465.820	55	15
6	1581.543	100	15

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	294	1597	benzene,m-dichloro-,
2	286	7524	benzenesulfonicacid,1-methyl-2,2,3,3-tetrafluoropropylester
3	266	535	pyridine,2-chloro-,
4	254	5856	ether,bis/2-/2,4,5-trichloro-phenoxy/ethyl/,
5	210	6989	ethanol,2-/2-/2-chloroethoxy/-ethoxy/-,
6	206	5600	acetaldehyde,2-phenoxy-,diethylacetal
7	142	3406	acetonitrile,methoxy-,
8	102	4579	methane,bromotrifluoro-,
9	86	5626	thiocyanicacid,4-hydroxy-2,3-xylylester
10	78	3023	s-triazine,2,4,6-tris-allyloxy/-,

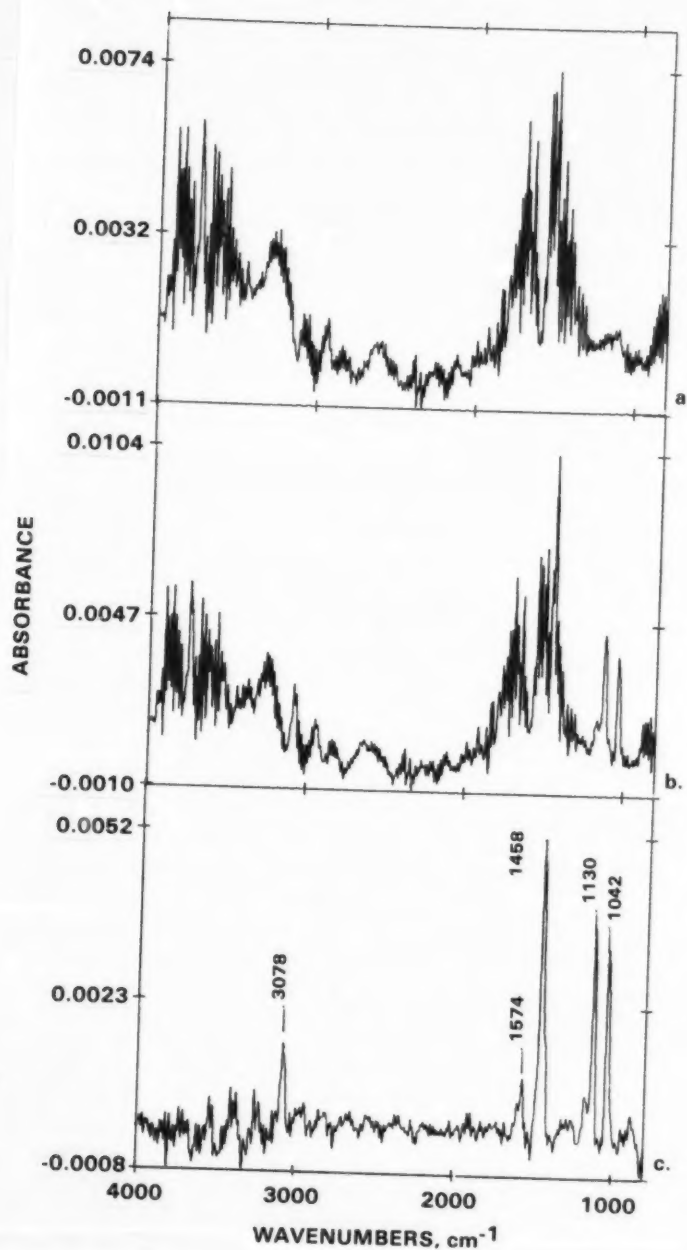


Figure 23. Peak 7, Figure 16 (o-dichlorobenzene)
 a. Absorption spectrum generated from baseline adjacent to peak interval (background correction).
 b. Uncorrected spectrum from peak interval.
 c. Corrected spectrum with peaks used for search identified.

TABLE 10

SADTLER SEARCH REPORT
PEAK 7, FIGURE 16 (O-DICHLOROBENZENE)

8 Peaks

Sensitivity: 80

<u>Peak No.</u>	<u>Energy (cm⁻¹)</u>	<u>Rel. Intensity</u>	<u>Width (cm⁻¹)</u>
1	887.207	8	23
2	1041.504	63	15
3	1130.225	70	23
4	1326.953	6	8
5	1458.105	100	31
6	1573.828	19	39
7	1897.852	7	15
8	3078.223	29	39

<u>Peak No.</u>	<u>Hit Quality</u>	<u>Spectrum No.</u>	<u>Compound Name</u>
1	310	125	benzene,o-dichloro-,
2	296	3174	acetonitrile,/methylimino/di-,
3	240	3529	picolinaldehyde,6-methyl-,o-benzyl-oxime
4	238	3616	thiocyanicacid,2-/2-butoxy-ethoxy/-ethylester
5	218	66	toluene,3,4-dichloro-,
6	218	5856	ether,bis/2-/2,4,5-trichloro-phenoxy/-ethyl/,
7	212	2111	phenothiazine
8	206	814	pyridine,2-chloro-6-ethoxy-,
9	206	1949	2-picoline,6-/2-methoxyethyl/-,
10	192	4686	ethanol,2-/2-/hexyloxy/ethoxy/-,

SECTION 6

DISCUSSION

1. The problem of water.--Water is not detected by the FID and thus is often not a serious problem in the application of GC to environmental analysis. However, the sensitivity of IR to the vibrational absorptions of water creates a significant complication for cartridge desorption GC/FTIR. TENAX-GC is normally thought of as a very poor adsorber of water and, in fact, can successfully be used to collect non-polar compounds, even in the presence of relatively high humidity³. However, it is clear from the preliminary parts of this work, that even when TENAX-GC is thoroughly purged at high temperatures and loaded under rigorously anhydrous conditions, there is sufficient water desorbed so that it still presents a problem for IR detection and identification. As shown in Figures 4-7 and 9-12, the addition of the Perma-Pure dryer significantly alleviates the water problem.

It should be noted, however, that the presence of water in the sample does not preclude the detection and identification of organic components. Comparing Figures 4 and 5, for example, it is clear that at high concentration, peaks can be observed even when they co-elute with the water band. On the other hand (as illustrated in Figures 9 and 10), for lower loadings still well within the detection and identification limits of the method, the water band substantially masks target peaks in the Gram-Schmidt trace. Figures 11 and 12 also show how (even when the target peak can be identified and analyzed) infrared bands are lost to the spectral saturation in the 1400 cm^{-1} region due to water absorption. It is also worth noting that (even in regions of the real-time chromatogram before and after the obvious "water band") the background is still primarily water. This is clearly illustrated by the substantial improvement of the spectra in Figures 17-23 after subtraction of background spectra, which have the water bands at 1400 and 3500 as their most prominent features.

The presence of water causes yet another significant complication in addition to the problem illustrated above. The Gram-Schmidt algorithm is designed so that in the auto-triggering mode interferograms are saved whenever the value of the computed point exceeds a threshold value. This is a practical necessity since there is not sufficient disk space to store all of the 9000 interferograms which are collected in a typical 30 min GC/FTIR run. If the effective base line is pushed above the threshold by the water "band", the auto triggering mode will cause continuous saving of interferograms. (Base line drift will have the same effect and was initially a serious problem; however, when operating properly the IBM 9195 should have a drift of less than $\pm 1\%$ over a 30 min period.) But even in the absence of baseline drift, the presence of water prevents the use of one of the attractive features of the method, i.e., automatic data collection. In fact, the data presented in this report were all collected by manually triggering interferogram storage in intervals anticipated to contain chromatographic peaks. In some instances identifiable spectra were even obtained by transformation of co-added interferograms from intervals showing no clearly discernible peak in the Gram-Schmidt trace. These intervals can be identified post facto by the appearance approximately four seconds later of a peak in the FID trace. At the present state of the system design, this requires two sample runs in order to be sure of storing all the relevant interferograms, using the FID retention times of the first run to identify peak intervals in the Gram-Schmidt trace of the second run. Clearly, this is not acceptable in the final system. Further improvements to the system which would allow the realization of the full automatic analytical potential of the method are proposed in the Recommendations Section.

The Gram-Schmidt trace in Figure 9 (which is representative of many similar runs) shows that water is a problem even when samples are loaded on and desorbed from previously dried TENAX-GC cartridges under rigorously anhydrous conditions. Apparently, IR-significant water is released by TENAX-GC during the thermal desorption process. Obviously water will be present when samples are taken from ambient air. The use of the Perma-Pure dryer reduces the water to manageable levels. However, it should be noted that the Nafion tubing of the dryer is also permeable to other polar

compounds such as pyridine. Consequently, use of the thermal desorption GC/FTIR method (as currently conceived) for detection and identification of polar organics will be severely limited.

2. Detection limits.-- Although the work on this project has not yet developed to the point of making a thorough study of detection limits for the various compounds of interest, it appears at this time that a rough estimate is in the region of 100 ng per compound per cartridge. A somewhat higher limit, probably near 400 ng, would be more realistic if the current system is to be used without further modification. At present the apparent practical limit on detection is the observation of the peaks in the Gram-Schmidt trace. The signal-to-noise ratio in the final spectra is approximately an order of magnitude greater than that of the real-time chromatogram. That is, if the time interval for saving and co-adding interferograms could be more easily recognized, detection limits could be significantly lowered. New methods of recognizing when peaks are, in fact, passing through the light pipe, are discussed in the Recommendations Section.

3. Identification of isomers.--The distinctive capability of GC/FTIR is the identification of geometrical isomers. Clearly the detection limits of GC/MS are lower, but, particularly in the case of closely eluting and co-eluting compounds and compounds of similar molecular weight and structure, GC/FTIR has an important role to play.

The results of the analysis of the mixture of isomeric chloro-organics shown in Table 3 is very illustrative of this capability. Although the peaks in the real-time FTIR chromatogram are very weak (Figures 15 and 16), they can be clearly identified with those in the FID trace (Figure 14). With the Perma-Pure dryer in place, all the compounds in the mixture elute after the residual water band. However, the subtraction of the (primarily water) background (Figures 17a-23a) from the raw spectra (Figures 17b-23b) gives extraordinarily well defined corrected spectra (Figures 17c-23c).

When these corrected spectra were subjected to the Sadtler library search, in only one case did the search fail to select the known compound in the ten best hits. From independent evidence (supplied by NSI) peak 1 (Figure 16) is known to contain both *m*-, and *p*-xylene with essentially no resolution between the two. The spectrum of the transform of the co-addition of all the interferograms "under" peak 1, as well as of those in the first or last half of the peak are essentially identical (Figure 17c). Since the bands of both isomers are present in the spectrum, the search (which presumes the spectrum is of a single compound) could not make a correct hit. Subtraction of a library spectrum of one or the other of the isomers from the spectrum of peak 1 would leave the peaks of the other isomer for very likely identification by standard search. It is necessary to establish a user-generated library for this purpose since it is not possible to do this subtraction with Sadtler library files. Ortho-xylene, which elutes separately, is identified from the corrected spectrum from peak 2 (Figure 18c) as hit 10 by the spectral search routine (Figure 18d).

Of the other isomer sets in the mixture, all are clearly identified. Particularly impressive is the generation of the separate isomer spectra of *o*-, *m*-, and *p*-chloro toluenes (Figures 19 to 21), despite the overlap of their peaks in both the FID and FTIR chromatograms (peaks 3-5). The spectra were obtained by co-adding interferograms from each of the components separately (#'s 3, 4 and 5). The ortho isomer is hit 7, the meta, hit 1, and the para, hit 2 when the background corrected spectra (Figures 19c-21c) of peaks 3, 4 and 5 are subjected to the standard search routine (Tables 6-8). Meta- and ortho-dichlorobenzene are both identified as hit 1 when the library is searched for the background corrected spectra of peaks 6 and 7. (Table 9 and 10).

These results are an excellent illustration of the importance of the background correction step in the treatment of the spectra prior to running the spectral search routine. For example, in Figures 22 and 23 the uncorrected spectra derived from peaks 6 and 7 appear to have only two small bands near 1100 cm^{-1} in both spectra (other than the water bands in the 1400 and 3500 cm^{-1} regions). The corrected spectra reveal several absorption peaks, all of which have a S/N ratio of more than 10 and, as mentioned above,

the spectral search identifies m- and o-dichlorobenzene as hit 1 in both searches.

Clearly these isomer identifications do not represent minimum detection limits. The loadings in this sample, 380-575 ng per compound, appear to be at least 2x the minimum reliable detection and identification limit. However, a more sensitive method of locating the Gram-Schmidt peaks is needed.

It should also be noted that, in this known mixture, the identity of each component in the chromatogram was previously established. Although the GC-FTIR data clearly distinguish between isomeric compounds (in that other isomers do not appear in the top 10 hits of the spectral search), completely general identification of these compounds from an unknown mixture would require consideration of other information, such as GC-retention times and GC-MS data.

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